

A Further Investigation
—OF THE—
Symmetrical Chloride of Paranitroortho-
sulphobenzoic Acid

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

—BY—

WILLIAM E. HENDERSON

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ACKNOWLEDGMENT.

The author esteems it a privilege, as well as a pleasure, to give expression to his sincere sense of gratitude to Professor Remsen, under whose guidance this work was carried on, not only for instruction received in the lecture room, but for his frequent suggestions, and his constant and friendly interest in the work as it progressed. These have at all times been an encouragement and an incentive.

He wishes also to express his appreciation of the instruction, and kindly guidance in the laboratory, of Drs. Morse and Renouf, as well as of Dr. Ames of the Physical Laboratory.

A FURTHER INVESTIGATION OF THE SYMMETRICAL CHLORIDE OF PARANITROORTHO-SULPHOBENZOIC ACID.

I. INTRODUCTION.

The sulphobenzoic acids have been the subject of investigation in this laboratory for a number of years past. Among the many interesting facts that have been brought to light in the course of this study, perhaps no other has been attended with more interest than the discovery of well characterized isomerism in the case of the chlorides of orthosulphobenzoic acid, and of its paranitro derivative, together with the preparation of a series of isomeric derivatives of these substances. The chlorides themselves have been isolated in crystalline condition, and have been found to differ markedly, not only in chemical, but in physical properties as well.

The first evidence that such isomerism existed, was obtained by Remsen and Coates¹ who, in the course of an investigation of the action of aniline upon the chloride of orthosulphobenzoic acid, obtained two isomeric anilides, quite different in properties, which they designated as fusible and infusible respectively. The following year, Remsen and Kohler² obtained one of the chlorides in crystalline form, together with an oil which they did not succeed in crystallizing. This, however, was accomplished the succeeding year by Remsen and Saunders,³ and a still more satisfactory result was obtained by Remsen and McKee,⁴ in 1895.

The chloride melting at 79° was found to yield only the fusible anilide, together with an anil, while from the lower melting chloride, in addition to these, the infusible anilid was also formed.

In 1895, Gray⁵ isolated the two corresponding isomeric chlorides of paranitroorthosulphobenzoic acid, the lower melting chloride being obtained in small quantity only. The suc-

¹ Am. Chem. J., 17, 311.

² Am. Chem. J., 17, 330.

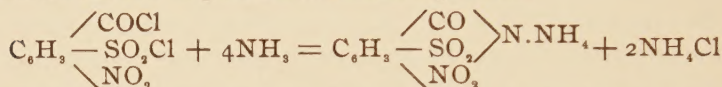
³ Am. Chem. J., 17, 354.

⁴ Am. Chem. J., 18, 794.

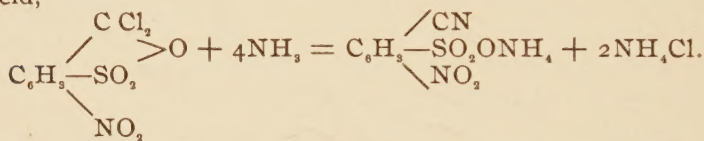
⁵ Inaug. Diss., J. H. U.

ceeding year, Hollis¹ made a more careful study of this lower melting chloride, and prepared it in considerable quantity.

From evidence drawn from the action of ammonia upon these chlorides, taken in connection with a number of other facts, the higher melting chloride is identified as the one possessing a symmetrical structure, while the lower melting chloride possesses an unsymmetrical structure. The first one when treated with ammonia is slowly transformed into the ammonium salt of paranitrobenzoic sulphinide.



while the lower melting chloride is quickly transformed into the ammonium salt of paranitroorthocyanbenzenesulphonic acid,



Gray's study of the symmetrical chloride was confined for the most part to the preparation of a series of salts of this latter acid, and to an investigation of the action of aniline upon the chloride itself. It was thought to be of interest to extend this study to a wider range of reactions, as well as to improve, if possible, the method of preparing the chloride in pure condition. At the suggestion of Professor Remsen this work was accordingly undertaken.

II. PREPARATION OF MATERIAL.

The method of preparation of paranitroorthosulphobenzoic acid employed, was essentially that described by Hart,² Kastle,³ Gray,⁴ and Hollis.⁵ The details of it are repeated here for the purpose of calling attention to certain facts that came under the author's notice.

100 grams of paranitrotoluene are added to 400 grams of fuming sulphuric acid, and the mixture heated in a balloon flask at 100° on a water-bath. The heating is continued un-

¹ Inaug. Diss., J. H. U.

² Am. Chem. J., 1, 350.

³ *Ibid*, 11, 177.

⁴ Inaug. Diss., J. H. U., 1896.

⁵ Inaug. Diss., J. H. U., 1896.

til a few drops of the mixture, added to cold water, dissolve completely to a clear solution. The time required for this operation varies much with the conditions. Continued stirring very considerably hastens the reaction, as paranitrotoluene forms a layer on the acid, which presents a small surface to its action. With constant stirring the reaction is complete in a few hours, whereas, if no stirring is resorted to, as much as several days is required, especially when large quantities are employed at one time.

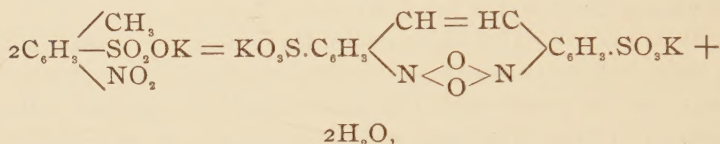
When the reaction is complete, the mixture is poured into a large volume of water and neutralized with calcium carbonate. In the filtrate from calcium sulphate the calcium salt of paranitroorthosulphotoluene is found, and this is converted into the potassium salt in the usual way.

The oxidation of the potassium salt is effected as follows: 50 grams of the salt are dissolved in 2.5 liters of water, and to this is added a solution of 15 grams potassium hydroxide. This mixture is heated to 100° on a water-bath, and when this temperature is reached 110 grams of potassium permanganate are added. Heating is continued until the solution is decolorized, care being taken to prevent the evolution of free oxygen. The oxides of manganese are then filtered off, the filtrate neutralized with hydrochloric acid, and evaporated to about a fifth of its original volume. Strong hydrochloric acid is added in excess, and on cooling the acid potassium salt of paranitroorthosulphobenzoic acid separates in very slender colorless needles, completely filling the liquid.

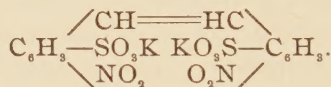
For the success of this operation it is important that the potassium salt of paranitroorthotoluenesulphonic acid and the potassium hydroxide should both be perfectly dissolved before they are heated together. If the two substances in solid form lie in contact at the bottom of the flask, a very slight elevation of temperature leads to the formation of an extremely troublesome red substance that is very difficult to remove. It is almost impossible to remove it from the oxidation product by recrystallization, since any considerable amount of it has a marked influence on the solubility of the salt, rendering it much more soluble. It persists throughout all the subse-

quent transformations of paranitroorthosulphobenzoic acid, and should therefore be carefully avoided.

Otto Fischer¹ has shown that in concentrated solution potassium hydroxide acts on nitro derivatives of toluene, with formation of various colored substances derived from stilbene. In the case of paranitroorthotoluenesulphonic acid, he describes the substance formed as possessing a cherry red color. The formation of the substance may be thus represented:



by oxidation this passes to a nitro compound of the composition



It was no doubt the formation of substances of this nature that occasioned the color observed in some of the oxidations. The only effective method of separating this colored substance was found to be to pass to the neutral salt of paranitroorthosulphobenzoic acid, by making the solution slightly alkaline. The salt of this colored substance is also formed, and the two can then be separated by a few crystallizations, in a fairly satisfactory manner.

The yield in both of the transformations involved in the preparation of paranitroorthosulphobenzoic acid does not fall far short of the theoretical.

III. PREPARATION OF THE SYMMETRICAL CHLORIDE OF PARANITROORTHOSULPHOBENZOIC ACID.

This chloride was first separated from its unsymmetrical isomer by Gray.² It was obtained by allowing a chloroform solution of the mixed chlorides to evaporate until the chloroform had almost entirely disappeared. In the thick liquid so obtained crystals of the symmetrical chloride were formed.

¹ Ber. d. chem. Ges., 26, 2231; 28, 2281.

² Inaug. Diss., J. H. U., 1895.

It was also obtained by applying the method devised by Bucher in connection with the corresponding chlorides of orthosulphobenzoic acid, *i. e.*, by the action of dilute ammonia on the mixed chlorides.

Gray also found that the best conditions for securing a relatively large proportion of the symmetrical chloride were the employment of as low a temperature as possible in the formation of the chlorides, and of as small an excess of phosphorus pentachloride as would suffice for the reaction.

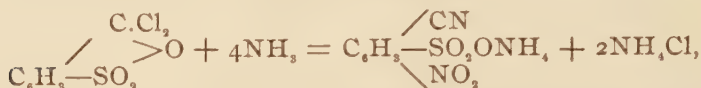
After many experiments, under widely different conditions, the following method of procedure, embodying the results of Gray's work, was adopted :

Dehydrated acid potassium salt of paranitroorthosulphobenzoic acid and phosphorus pentachloride, in the ratio of 40 : 55 grams, are brought together in a mortar and intimately mixed. The mixture is put into an evaporating dish and placed on a sulphuric acid bath, previously heated to 150°. As soon as the action has been well started, the dish is removed and the reaction allowed to proceed without further heating. When it is complete, and the contents of the dish has cooled down to the ordinary temperature, the oily product is poured slowly into a salts bottle containing ice water, the bottle being frequently shaken during the process. The chloride is then shaken with repeated portions of water, until the water remains clear after shaking, and the chloride has become semi-solid. The water is then poured off, the brownish gummy chloride dissolved in chloroform, and the solution placed in a good-sized separating funnel. Ice water is then added, and the contents of the funnel treated with successive portions of ammonia (desk ammonia diluted one-half). Shaking is continued after each addition until the odor of ammonia has disappeared, and ice is added from time to time as may be required.

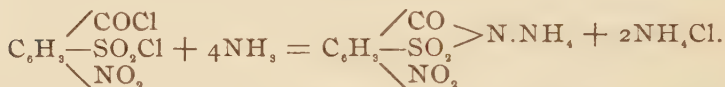
When it is found that the odor of ammonia persists after a few minutes' shaking, the chloroform layer, which is often filled with a solid substance that has separated during the process, is drawn off, filtered, and dried with calcium chloride.

By this process all of the unsymmetrical chloride is con-

verted into the ammonium salt of paranitroorthocyanbenzenesulphonic acid, according to the equation:



while the unsymmetrical chloride remains for the most part unchanged, though some of it is converted into the ammonium salt of paranitrobenzoicsulphinide



It was found that working in this way the symmetrical chloride could be prepared in pure condition free from its isomer. The chloroform completely evaporates in a short time, leaving fine crystals of the symmetrical chloride. In case the evaporation is slow and incomplete, it may be concluded that not all of the unsymmetrical chloride has been removed. The yield was uniformly about 40 per cent. of the theoretical.

From the water used to wash the chlorides a considerable amount of the original salt may be regained, as the reaction, under the conditions employed, is never complete.

An examination was made of the substance mentioned as separating in the chloroform solution of the chlorides during the treatment with ammonia, and it was found to possess the following properties. It is insoluble in benzene, chloroform, acetone, ether, and ligroin; soluble in glacial acetic acid, from which it separates, on cooling, in colorless crystalline condition; insoluble in the cold in water, alcohol, and ammonia, but by long standing in these solvents it is dissolved with decomposition. It is soluble in them on boiling, with decomposition. It was dissolved in hot water, and the solution, which was acid in reaction, was neutralized with potassium carbonate. On adding an excess of hydrochloric acid to this solution and allowing it to cool, characteristic needles of the acid potassium salt of paranitroorthosulphobenzoic acid separated. These properties identify the substance as the anhydride of this acid. The formation of the corresponding anhydride of orthosulphobenzoic acid by the action of phosphorus

pentachloride upon its acid potassium salt was observed by Sohon,¹ who made use of the reaction to prepare this anhydride in quantity.

IV. PROPERTIES OF THE SYMMETRICAL CHLORIDE OF PARANITROORTHOSULPHOBENZOIC ACID.

As first obtained, the crystals of the symmetrical chloride resemble irregularly shaped pieces of amber, both in color and in lustre. On recrystallization from chloroform or ether they may be obtained perfectly colorless, and are often of very simple crystallographic form. The chloride crystallizes in the monoclinic system, and possesses a very remarkable crystallizing power, in which respect it differs noticeably from its isomer. Even in chloroform solution that is far from dry, crystals appear with the greatest ease.

The habit of the crystals differs very much according to the conditions of crystallization. Not infrequently almost perfectly formed crystals of the simplest form—the oblique octahedron—were obtained, though for the most part the form was much more complicated, pinacoid and dome faces, together with basal planes, being prominent. As a rule, the crystals were not suitable for crystallographic work, as the faces are rough, owing to the great solubility of the chloride. By proper precautions, however, fairly good ones were obtained for this purpose. The size of some of the crystals obtained was unusual for substances of this class. One crystal obtained with no special precautions, save letting a solution of the chloride stand undisturbed for several days, in a rather cool place, measured $3 \times 2.5 \times 1.5$ cm., and weighed 11.2 grams.

The crystals are quite compact, their density being about 1.85. They melt at 98° (uncorr.). The chloride is quite stable when crystallized. Even in moist air the crystals were unchanged and retained their lustre as long as they were in my possession.

An analysis for chlorine gave the following results :

0.2200 gram gave 0.2212 gram AgCl .

	Calculated for	
	$\begin{array}{c} \text{COCl} \\ \diagup \\ \text{C}_6\text{H}_3-\text{SO}_2\text{Cl} \\ \diagdown \\ \text{NO}_2 \end{array}$	
Cl	24.94	Found. 24.83

¹ Inaug. Diss., J. H. U., 1896.

A crystallographic examination of the usual form of the crystals was made by Dr. F. P. King, in the mineralogical laboratory, and his measurements and description are here given :

System monoclinic.

$$s = +\frac{1}{2}P\infty = (201)$$

$$o = +P = (111)$$

$$c = +P\infty = (011)$$

$$m = \infty P = (110)$$

$$s : m' = 97^{\circ} 35'$$

$$s : o = 120^{\circ} 26'$$

$$s : c = 132^{\circ} 45'$$

$$o : o = 96^{\circ} 20'$$

$$o : c = 138^{\circ} 10'$$

$$o : m' = 87^{\circ} 31'$$

$$o : m = 138^{\circ} 01'$$

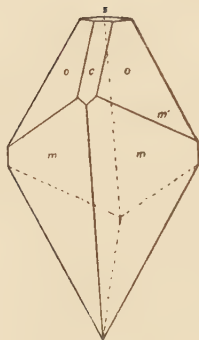
$$m : m = 116^{\circ} 50'$$

$$m : m' = 63^{\circ} 10'$$

$$m : c = 122^{\circ} 19'$$

$$a : b : c :: 0.898321 : 1 : 1.114179$$

$$\beta = 43^{\circ} 11' 17''$$



The figure is drawn on Dana's axes, showing β in front. Distortion, due to irregular growth, causes planes c and s to generally disappear at one extremity of c axis.

Since merohedrism is invariably present in respect to these planes the figure is drawn conformable to this distortion.

The measurements given are the actual measurements.

V. THE ACTION OF ALUMINIUM CHLORIDE AND BENZENE UPON THE SYMMETRICAL CHLORIDE OF PARANITRO-ORTHOSULPHOBENZOIC ACID.

Hollis,¹ in his study of the action of these reagents upon the unsymmetrical chloride, tested their action upon one portion of the symmetrical chloride, and found the products to be identical in the two cases. A few experiments were made in confirmation of these results, and the same products, in gen-

¹ Inaug. Diss., J. H. U., 1896.

eral, were obtained. It was observed, however, that the reactions differ in the relative ease with which they are brought about. In the case of the symmetrical chloride, the reaction is a more vigorous one. On adding aluminium chloride to a solution of the symmetrical chloride in benzene, action begins at once at the temperature of the hand, and very little external heat, and that only in the latter stages of the operation, is required to complete the reaction. The application of much heat converts all of the product into thick tarry substances, from which nothing satisfactory could be obtained.

When the reaction was complete, the resulting product was isolated and purified in accordance with the directions given by Hollis. Repeated trials showed that, as in the case of the unsymmetrical chloride, only one phenyl group could be introduced by this method. The resulting compound, paranitroorthobenzoylbenzenesulphone chloride, was identical with that derived from the unsymmetrical chloride. Owing, however, to the fact that so much more decomposition occurs in the reaction with the symmetrical chloride, the paranitroorthobenzoylbenzenesulphone chloride could not be obtained in perfectly pure condition. In appearance it agreed closely with that described by Hollis, forming very characteristic, greenish, rhombic crystals. These melted, not very sharply, at 174° instead of 177° , as observed by Hollis. Accordingly, to establish the identity of the two compounds, beyond any doubt, the material on hand was converted into the barium salt of paranitroorthobenzoylbenzenesulphonic acid. This was done by boiling the sulphone chloride with dilute hydrochloric acid until complete solution was effected; evaporating to dryness on a water-bath, dissolving the residue in hot water, and neutralizing with barium carbonate. On filtering the hot solution, and allowing it to cool, the barium salt separated.

The solution was slightly colored by impurities and the long needles in which the salt crystallized were also somewhat colored. They were analyzed with the expectation that they would prove to be specimens of the salt described by Hollis as having three or three and a half molecules of water of crystallization, inasmuch as they were formed under con-

ditions favorable to the formation of salts of this particular type. Hollis found that this salt could be obtained with at least four different ratios of water of crystallization, *viz.*, three, three and a half, six, and seven molecules, respectively. The analysis was as follows :

0.3087 gram lost 0.064 gram H_2O at 210° , and gave 0.0759 gram BaSO_4 .

	Calculated for $(\text{C}_{12}\text{H}_8\text{O}_6\text{NS})_2\text{Ba} + 11\text{H}_2\text{O}$.	Found.
H_2O	20.90	20.73
Ba	18.29	18.23

The mother liquor, in which the crystals remaining from analysis were redissolved, was warmed, but not boiled, with bone-black to remove impurities. When filtered the solution was perfectly colorless, and on standing for some time, well formed, colorless, rhombic crystals appeared.

On analysis they gave the following results :

0.2804 gram lost 0.0405 gram at 210° , and gave 0.0736 gram BaSO_4 .

	Calculated for $(\text{C}_{12}\text{H}_8\text{O}_6\text{NS})_2\text{Ba} + 7\text{H}_2\text{O}$.	Found.
H_2O	14.40	14.44
Ba	18.29	18.03

In making a further supply of the salt it was found that if the solution, after filtering from the excess of barium carbonate, was diluted to such an extent that no crystals separated on cooling, then, on slow evaporation under a bell jar, the first crystals to appear were very long needles. As evaporation proceeded these needles became much thicker, assuming prismatic proportions, and corresponded in appearance to the salt described by Hollis as having six molecules of water of crystallization. As growth proceeded the crystals became dark in color, and the mother liquor correspondingly clearer. Evidently the crystals absorbed the colored impurities in their growth. When the solution had become quite colorless, rhombic crystals of the salt containing seven molecules of water of crystallization appeared. The larger prismatic crystals were carefully removed, and redissolved in water in order to see if the same phenomena would repeat themselves. This was in fact found to be the case, crystals of both types re-

sulting. Without separating the crystals in this second experiment, water was added, and the crystals dissolved. The solution was then warmed briskly with bone-black, and filtered. From the filtrate, which was now colorless, nothing but the rhombic crystals having seven molecules of water of crystallization could be obtained, although the conditions were widely varied.

Analysis of these last crystals gave the following results :

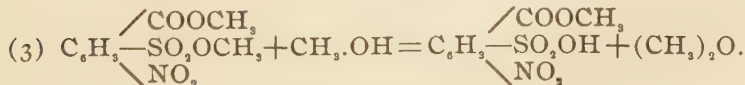
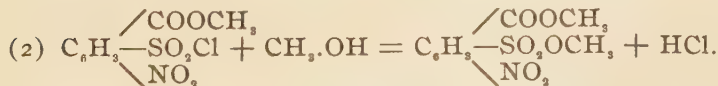
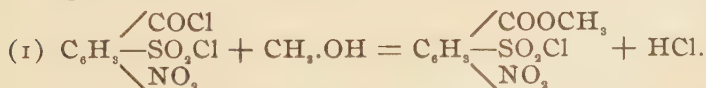
0.2400 gram lost 0.035 gram at 210° , and gave 0.0637 gram BaSO_4 .

	Calculated for $(\text{C}_{13}\text{H}_8\text{O}_6\text{NS})_2\text{Ba} + 7\text{H}_2\text{O}$.	Found.
H_2O	14.40	14.58
Ba	18.29	18.27

Hollis states that boiling with bone-black decomposes this salt, and hence he did not attempt to purify it prior to crystallization. From the experiments just described it seems probable that the impurities present affect the crystalline habit, and the degree of hydration of this salt in a very striking manner. By careful warming with bone-black no decomposition was observed, and the crystals obtained from such a solution were always constant in properties, having seven molecules of crystal water.

VI. ACTION OF ALCOHOLS UPON THE SYMMETRICAL CHLORIDE OF PARANITROORTHOSULPHOBENZOIC ACID.

Kastle¹ found that when the chloride of paranitroorthosulphobenzoic acid (which he supposed to be an individual) was dissolved in alcohol and the solution boiled for some time, the acid ethereal salt of paranitroorthosulphobenzoic acid was the final product.



¹ Am. Chem. J., 11, 181.

Kastle, it will be observed, gave the symmetrical formula to this mixture of chlorides. Several acid-ethereal salts were made, and a series of neutral salts of various metals described by him.

The action of the pure symmetrical chloride was studied in the same general manner, to see if the resulting products would be the same as those resulting from the mixed chlorides.

1. *The Action of Methyl Alcohol upon the Symmetrical Chloride.*

A portion of the chloride was dissolved in methyl alcohol and the solution boiled until a drop added to water gave no precipitate of unchanged chloride. The alcohol was then distilled off, and the thick syrup remaining diluted with water. This was neutralized with barium carbonate and filtered. On cooling the barium salt crystallized in shining mica-like plates, or in yellowish needles corresponding accurately with the description given by Kastle. Analysis:

0.2664 gram lost 0.0211 gram H_2O at 150° , and gave 0.0870 gram $BaSO_4$.

	Calculated for	Found.
	$\left(C_6H_5 \begin{array}{c} \nearrow COOCH_3 \\ \text{---} SO_2O \\ \nwarrow NO_2 \end{array} \right)_2 Ba + 3H_2O.$	
H_2O	7.59	7.88
Ba	20.85	20.85

2. *The Action of Ethyl Alcohol upon the Symmetrical Chloride.*

In like manner the barium-ethyl salt was made. It also agreed perfectly with Kastle's description, crystallizing in fine, colorless needles forming tufts, from a not too concentrated solution. In case it is necessary to concentrate these solutions it is of advantage to add a small quantity of alcohol to the solution, as this prevents any great amount of saponification, which otherwise takes place to a noticeable extent. Analysis:

I. 0.2824 gram lost 0.0276 gram at 180° , and gave 0.0860 gram $BaSO_4$.

II. 0.2655 gram lost 0.0262 gram H_2O at 190° , and gave 0.0815 gram $BaSO_4$.

Calculated for			
$\left(\text{C}_6\text{H}_5 \begin{array}{l} \nearrow \text{COOC}_2\text{H}_5 \\ \text{—SO}_2\text{O—} \\ \searrow \text{NO}_2 \end{array} \right)_2 \text{Ba} + 4\text{H}_2\text{O}.$			
		I.	Found. II.
H ₂ O	9.51	9.77	9.86
Ba	20.00	19.84	20.02

Kastle also found that by dissolving the mixed chlorides in cold alcohol, and allowing the solution to evaporate spontaneously, there separated crystals of the chloride of the acid ethereal salt of paranitroorthosulphobenzoic acid represented in equation (1). This same product was sought for, when pure symmetrical chloride was employed, but without success. Under all conditions crystals of unchanged chloride separated, or else it was found that it had been converted into the acid ethereal salt. In another trial, cold water was carefully added in small portions, since Kastle found that such treatment facilitated the separation of the substance; the chloride alone appeared. Still other attempts were made to obtain the substance by adding a large amount of water to the solution of the chloride in alcohol, after it had stood for some time. In this way quite a precipitate was thrown down, and this was filtered off and crystallized from ether. It always proved to be the symmetrical chloride, and none of the other substance was obtained.

Karslake,¹ in working with the symmetrical chloride of orthosulphobenzoic acid, was unable to isolate the analogous compound, although from the mixed chlorides, by the action of alcohols, Remsen and Dohme² had obtained chloroethereal salts.

Inasmuch as the pure symmetrical chloride is relatively stable in cold alcohol, it can even be crystallized from warm alcohol with very little loss; it is possible that it is more stable than the chloro-ethereal salt, and that in consequence the latter, when formed, yields more readily to the further action of the alcohol than does the unacted-on chloride. Hence, when the action begins it at once proceeds to the limit. The fact that the symmetrical chloride is rather sparingly soluble in cold alcohol, making the use of a concentrated solution impossible, may also be a factor in the case. Whatever may be

¹ Inaug. Diss., J. H. U., 1895.

² Am. Chem. J., II, 341.

the cause, the substance could not be obtained under any conditions that were devised.

Having in my possession a very small specimen of crystallized unsymmetrical chloride, it was submitted to the action of ethyl alcohol, under as nearly as possible the conditions employed by Kastle.

Crystals of a colorless substance were obtained, which in every respect agreed with Kastle's description of the chloride of the acid ethyl ethereal salt of paranitroorthosulphobenzoic acid. Crystallized from ether, they melted at 68°.

The conditions employed by Kastle in preparing the chloride would undoubtedly lead to a relatively large proportion of the unsymmetrical chloride, and it is to this chloride that the formation of the chloro-ethereal salt is apparently due.

VII. THE ACTION OF PHENOLS UPON THE SYMMETRICAL CHLORIDE OF PARANITROORTHOSULPHOBENZOIC ACID.

Remsen and Saunders,¹ in their investigation of the chlorides of orthosulphobenzoic acid, studied the action of phenol upon these substances, and from both the symmetrical chloride and the mixed chloride; they obtained a normal diphenyl ether, and a red substance which was not further studied. It was formed in small quantity, and was probably the corresponding sulphonphthaleïn. Later Remsen and McKee² obtained these same substances from both the symmetrical and unsymmetrical chlorides of the same acid. R. Meyer³ obtained analogous substances by the action of various phenols upon phthalyl chloride. It seemed probable, therefore, that the chlorides of paranitroorthosulphobenzoic acid would yield similar derivatives, and a study was made of the reaction of the symmetrical chloride with a series of phenols. The products in some instances were exceedingly difficult to deal with, possessing properties that made it impossible to prepare them for analysis, but even in such cases there could be little doubt as to the general nature of the reactions which had occurred.

¹ Am. Chem. J., 17, 347.

² Am. Chem. J., 18, 798.

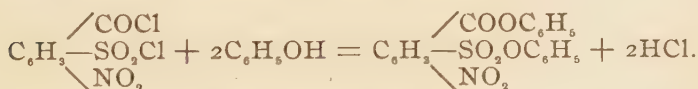
³ Ber. d. chem. Ges., 26, 204.

1. *The Action of Phenol upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.*

A portion of the symmetrical chloride was brought together with somewhat more than double the molecular amount of phenol. The mixture was placed in a good-sized test-tube, and the temperature gradually raised by means of a sulphuric acid bath. As soon as the phenol melts some slight action occurs, as is indicated by the bright red color which the liquid assumes. No appreciable amount of hydrochloric acid gas is evolved, however, until the mixture has reached a temperature of about 115° . At this point the gas is freely evolved, and the action is complete at 125° . The temperatures were ascertained by the use of a thermometer as a stirring rod. During the heating the color becomes a much more intense red, growing darker in shade, while the mixture becomes somewhat viscous, but does not solidify while hot.

When cool, the solid product was repeatedly extracted with boiling water, the aqueous solution being very deep purple in color. The colored material was very slowly removed from the insoluble residue in this manner, and so the process was continued with dilute alkali. The solid residue was dissolved in alcohol, purified with bone-black, and filtered. On cooling, needles of a straw-yellow color separated, which melted at 119° (uncor.).

These proved to be the normal diphenyl ethereal salt of paranitroorthosulphobenzoic acid, the formation of this substance being expressed by the equation:



Analysis of the substance gave the following results:

I. 0.1627 gram gave 0.3398 gram CO_2 and 0.0510 gram H_2O .

II. 0.1999 gram gave 0.4180 gram CO_2 and 0.0600 gram H_2O .

III. 0.2649 gram gave 0.1561 gram BaSO_4 .

	Calculated for $\text{C}_6\text{H}_3\text{—}\begin{array}{c} \diagup \text{COOC}_6\text{H}_5 \\ \text{—SO}_2\text{OC}_6\text{H}_5 \\ \diagdown \text{NO}_2 \end{array}$	I.	Found. II.	III.
C	57.14	56.97	57.03	
H	3.26	3.47	3.33	
S	8.02			8.09

The substance possesses properties similar to those of the diphenyl ethereal salt of orthosulphobenzoic acid described by Saunders. It is insoluble in water, and is unaffected by hydrochloric acid or aqueous alkali. On heating for a short time with alcoholic potash the needles were transformed into a voluminous precipitate. This was filtered off, dissolved in water, and hydrochloric acid was added. On cooling, characteristic crystals of the acid potassium salt of paranitroorthosulphobenzoic acid separated. Analysis:

0.1392 gram lost 0.009 gram at 150° and gave 0.0385 gram K_2SO_4 .

	Calculated for $\text{C}_6\text{H}_3\text{—}\begin{array}{c} \diagup \text{COOH} \\ \text{—SO}_2\text{OK} \\ \diagdown \text{NO}_2 \end{array} + \text{H}_2\text{O}$	Found.
H_2O	5.95	6.51
K	13.65	13.35

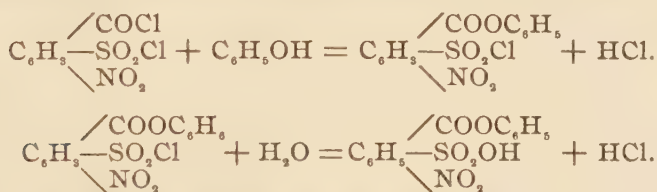
No attempt was made to isolate the intermediate chloro-ethereal salt of the composition $\text{C}_6\text{H}_3\text{—}\begin{array}{c} \diagup \text{COOC}_6\text{H}_5 \\ \text{—SO}_2\text{Cl} \\ \diagdown \text{NO}_2 \end{array}$ or its amide as was done by McKee¹ in his work on the analogous ethereal salt of orthosulphobenzoic acid.

On evaporating the aqueous extract from the original insoluble residue almost to dryness on the water-bath, there was a deposit on the sides of the dish of scales possessing a beautiful bronze-green metallic lustre. They formed a deep purple solution in alkalis, or magenta, if the solution was very dilute, and orange-yellow in acids. On acidifying the alkaline extract with hydrochloric acid, this same substance was precipitated as a brownish, flocculent precipitate. It was, however, found to be impossible to obtain this substance in pure condition. The amount formed in the reaction is small, and its properties were such as to render work with it

¹ Am. Chem. J., 18, 799.

very difficult. The method of preparation is not satisfactory because, owing to the fact that the substance is soluble in acid solutions to an unusual extent for substances of this class, the solution had to be concentrated to such a degree as to render the precipitated substance very impure from acids and alkali salts. These could not be washed out, obviously, without again dissolving the substance. From its properties, however, and its color reactions, there can be little doubt that the substance is a sulphonphthaleïn, and that it is always formed in considerable quantities in the reaction of phenol upon the symmetrical chloride.

It was noticed that the aqueous extract of the mass left after fusion was almost always decidedly acid in reaction, and it was thought that this might be due to the formation of an acid ethereal salt, whose formation could be thus expressed :



Accordingly, the solution was saturated with barium carbonate, the excess of carbonate removed by filtration, the filtrate concentrated, and allowed to cool. Crystals, in the form of pearly scales, separated, which upon analysis proved to be the neutral barium salt of paranitroorthosulphobenzoic acid.

0.2291 gram anhydrous salt gave 0.1386 gram BaSO_4 .

	Calculated for	
	$\text{C}_6\text{H}_5\begin{array}{c} \diagup \text{COO} \\ \text{—SO}_2\text{O} \\ \diagdown \text{NO}_2 \end{array} > \text{Ba}.$	
Ba	35.85	Found.
		35.57

This would seem to indicate that the reaction is an incomplete one, even in the presence of an excess of phenol. No indication of an acid ethereal salt was observed.

2. The Action of Orthocresol upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.

With orthocresol the reaction proceeds with more difficulty

A higher temperature was required (135° – 145°), and quite an amount of tarry material was obtained from which very little could be extracted. The product was warmed repeatedly with dilute alkali, the solution so obtained neutralized with hydrochloric acid, and distilled with steam for several hours to free it from cresol. The resulting solution was then evaporated to small volume, and acidified with hydrochloric acid. A considerable precipitate was thrown down, which was easily filtered off and dried. In this condition it was a dark purple-red powder, lumps of which possessed a yellowish-bronze metallic luster. In dilute alkaline solution it forms a deep bluish-purple solution, while in acids it is crimson, or light yellow if the solution is very dilute. It is an excellent indicator, especially with ammonia.

In the insoluble tarry substance the ethereal salt was sought for and obtained in small quantity only. As all of the tarry substance is soluble in alcohol and separates again from it on cooling, in much the same condition, the ethereal salt could not be isolated by crystallization from this solvent. By boiling the substance with benzene, purifying the filtrate with bone-black, and allowing the benzene to evaporate, an almost colorless, gummy substance was obtained, which, when dissolved in alcohol, crystallizes in small, colorless needles, which melt at 89° – 90° . They were not obtained in quantity sufficient for analysis, but there was no doubt that they were crystals of the diorthocresol ethereal salt.

Apparently much more decomposition occurred in this reaction than when paracresol was employed, probably in consequence of the higher temperature required for the reaction.

3. *The Action of Paracresol upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.*

This reaction was conducted in the same manner as with phenol. No hydrochloric acid was evolved until a temperature of about 110° was reached, although after melting, the solution had steadily darkened to a deep reddish-brown color. At 130° , after heating for several hours, hydrochloric acid ceased to be evolved. The product was treated as in the last experiment. The alkaline extract did not exhibit any

marked color reactions, such as were observed in most of these experiments, being dull reddish-brown in both acid and alkaline solution.

The insoluble residue crystallized from alcohol in light brownish transparent crystals, which did not lose their color by repeated crystallization and boiling with bone-black, and which melted at 117° . From benzene they crystallized in colorless needles or flat narrow plates. These became opaque on exposure to the air, apparently through loss of benzene of crystallization. Analyses:

I. 0.2372 gram of the substance gave 0.5137 gram CO_2 and 0.0965 gram H_2O .

II. 0.2223 gram gave 0.1203 gram BaSO_4 .

	Calculated for $\text{C}_6\text{H}_3\text{—}\begin{array}{l} \diagup \text{COOC}_6\text{H}_4\cdot\text{CH}_3 \\ \diagdown \text{SO}_2\text{OC}_6\text{H}_4\cdot\text{CH}_3 \\ \text{NO}_2 \end{array}$	I.	Found.	II.
C	59.08	59.06		
H	3.98	4.52		
S	7.49			7.43

4. *The Action of Hydroquinone upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.*

Action with hydroquinone occurs at 120° – 135° , the mixture at the same time becoming dark colored and viscous. On cooling, the product was powdered and treated with dilute alkali. It readily dissolved, without residue, forming a dark red solution. In concentrated solution the addition of acid produces a voluminous precipitate, dark brown in color, which when washed and dried on paper forms an almost black powder. A dilute solution of this powder is dark red when alkaline, orange-yellow when acid.

From the way in which this powder was obtained, and owing to the fact that its solubility prevented repeated washing, it was evident that it would not give close analytical results for a calculated formula. It was thought, however, that analysis would give a general idea of the composition.

Analysis of different specimens gave results for sulphur, which averaged about 5.5 per cent. The percentage required

for the formula $\text{C}_6\text{H}_3-\begin{array}{c} \diagup \\ \text{SO}_2 \\ \diagdown \\ \text{NO}_2 \end{array} \begin{array}{c} \text{C} [\text{C}_6\text{H}_3(\text{OH})_2]_2 \\ >\text{O} \end{array}$, which represents

the simplest fluoresceïn, is 7.43. The compound could hardly have been so far from pure as to occasion such a discrepancy in results as this. It would appear, therefore, that more than two molecules of hydroquinone enter into reaction with one molecule of the chloride. Should four molecules be involved in the reaction, leading to a compound of some such formula

as $\text{C}_6\text{H}_3-\begin{array}{c} \diagup \\ \text{SO} [\text{C}_6\text{H}_3(\text{OH})_2]_2 \\ \diagdown \\ \text{NO}_2 \end{array} \begin{array}{c} \text{C} [\text{C}_6\text{H}_3(\text{OH})_2]_2 \\ >\text{O} \end{array}$, the theoretical percentage of sulphur would be 6.00, which corresponds much more closely with the results obtained.

This is in accord with the observations of a number of workers in this laboratory—Lyman, Gilpin, Linn, and others—who have worked on various sulphonfluoresceïns, and have found that in many cases, four, six, and even eight phenol residues condense with one molecule of the anhydrous acid. Lyman¹ especially describes a tetrahydroquinone sulphonfluoresceïn derived from orthosulphoparatoluic acid. No ethereal salt was observed.

5. *The Action of Resorcin upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.*

The reaction of the chloride with resorcin is a much cleaner one and proceeds more readily than in the cases just described, leading, apparently, to an individual, well characterized compound. During the reaction, which is complete at 125°, the mixture becomes almost perfectly solid, and, when cool, is quite brittle. It was reduced to a reddish powder and dissolved in sodium hydroxide, there being no insoluble residue. By the addition of an acid, the sulphonfluoresceïn was thrown down as a chocolate brown precipitate.

This was washed repeatedly by decantation and upon the filter, and was finally collected and dried on drying paper. In this condition it is a light chocolate-brown powder. In

¹ Am. Chem. J., 16, 525.

dilute alkaline solution it possesses a slight fluorescence, being pink by transmitted and yellow by reflected light, suggesting eosin in a general way. It is interesting to note that the sulphonfluorescein of orthosulphobenzoic acid possesses a fluorescence which is almost indistinguishable from ordinary fluorescein, and that the introduction of a nitro group into the acid residue affects the color very much as the introduction of four bromine atoms into fluorescein. In acid solution the color is reddish-orange. Analysis of the compound gave the following results:

- I. 0.1745 gram gave 0.3339 gram CO_2 and 0.059 gram H_2O .
 II. 0.1467 gram gave 0.2820 gram CO_2 and 0.0432 gram H_2O .
 III. 0.1732 gram gave 0.3345 gram CO_2 and 0.0571 gram H_2O .
 IV. 0.2000 gram gave 0.1104 gram BaSO_4 .
 V. 0.1505 gram gave 0.0820 gram BaSO_4 .

Calculated for $\text{C} \left[\text{C}_6\text{H}_3 \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix} \right]_2$ $\text{C}_6\text{H}_5 \begin{smallmatrix} \text{SO}_2 \\ \text{NO}_2 \end{smallmatrix}$						
		I.	II.	Found. III.	IV.	V.
C	52.66	52.18	52.42	52.67		
H	3.46	3.76	3.27	3.66		
S	7.39				7.57	7.48

An effort to obtain the anhydride was not successful. Some loss of weight was observed, but before the loss corresponded to one molecule of water, the substance underwent decomposition.

6. *The Action of Pyrogallol upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.*

The product of this action dissolves readily in alkali, producing a very deep purple-black color in concentrated solution, passing to grayish-violet as the solution is diluted. On the addition of acid it was precipitated as a black gelatinous mass. On attempting to collect the precipitate, it forms a sticky black mass, which cannot be filtered successfully. It is best to evaporate to dryness, before filtration, and powder

the residue. The powder can then be washed fairly clean. No ethereal salt was formed.

An analysis for sulphur showed that in this gallein, as in the case of the phthalein derived from hydroquinone, more than two pyrogallol residues had entered the acid residue. The indications were that six molecules had entered into one of the chlorides. This also agrees with the observation of Lyman,¹ who describes a hexapyrogallol gallein of orthosulphoparatoluic acid. Probably a mixture of varying composition was obtained, and little importance was attached to the results save as they showed that no ethereal salt was formed in the reaction.

7. *The Action of β -Naphthol upon the Symmetrical Chloride of Paranitroorthosulphobenzoic Acid.*

It was hoped that here, as in the case of monohydroxy phenols, an ethereal salt would be obtained. It was found, however, that very little action occurred, save such as was indicated by the development of a bright carmine color, until a temperature of 160° was reached. At this point hydrochloric acid was evolved, but the chloride itself undergoes decomposition. Nothing definite could be isolated among the reaction products, save unchanged β -naphthol.

X. ACTION OF ANILINE ON THE SYMMETRICAL CHLORIDE OF PARANITROORTHOSULPHOBENZOIC ACID.

As has been pointed out in the introduction, it was in connection with the aniline derivatives of orthosulphobenzoic acid that isomerism of the chloride was first noticed, two anilids being obtained. Accordingly, when Gray began his study of the chlorides of paranitroorthosulphobenzoic acid, his first effort was to obtain evidence of the existence of two anilids. These were not obtained, however, until after the chlorides themselves had been isolated, as their properties made their preparation and isolation a matter of some difficulty. Some points still remained unsettled from Gray's study, and a further investigation was deemed advisable to clear these up.

Some time was spent in an endeavor to obtain a method by

¹ Am. Chem. J., 16, 527.

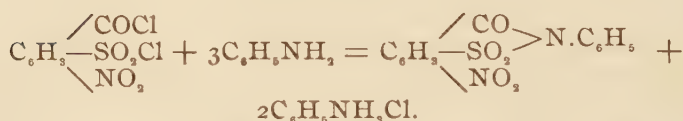
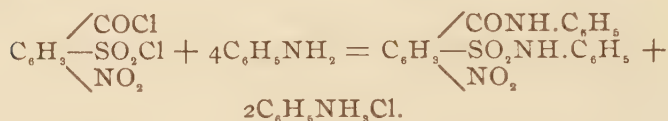
which a good yield of the fusible or symmetrical anilid could be obtained. The yield in all cases tried is not a good one. The presence of the nitro group appears to complicate the reaction, leading to secondary reaction, whose course could not be followed. Upon bringing aniline and the chloride together a very vivid color was always observed, and the same was true when it was necessary to employ alkali. The fact that such colors develop when nitro compounds are treated with alkali has been noticed in many instances, and some progress has been made in the study of these compounds. Jackson and Ittner¹ have recently reviewed this subject. If a solution of the symmetrical chloride in ether is slowly added to a similar solution of aniline, no appreciable amount of heat is generated. If the resulting solution is allowed to stand at the temperature of the room, action proceeds very slowly. The extent to which the action has progressed may be followed by observing the amount of aniline hydrochloride precipitated, as the other products of the reaction are soluble in ether. In this way it was found that five grams of chloride required about fifty hours for its conversion into anilid and anil. Results of an entirely similar character were obtained with chloroform as the solvent. By boiling the solution for an hour or so the reaction is complete.

The method employed was to bring the chloride and an excess of aniline—somewhat more than four molecules—together in chloroform solution. The flask was then boiled for about an hour, after which the chloroform was distilled off. During the boiling, as well as the distillation, more or less bumping occurs in consequence of the aniline hydrochlorid which separates, and constant shaking of the flask is sometimes necessary. The residue, which is in a thick, gummy condition, in consequence of the presence of an excess of aniline, was digested with water acidulated with hydrochloric acid. The excess of aniline is thus removed and the reaction product obtained as a reddish-brown solid substance. This was treated with dilute sodium hydroxide, in the cold, all lumps of the solid substance being broken up with a stirring rod. The undissolved substance is largely anil, which was filtered off.

¹ Am. Chem. J., 19, 199.

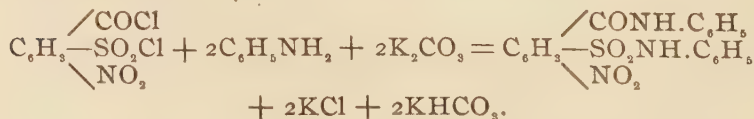
The anilid, which is in solution, is obtained by acidifying the alkaline solution. It separates immediately as a curdy colorless precipitate, though it is frequently discolored by impurities. In such a case it was frequently easily purified by re-dissolving in alkali and pouring this solution into a slight excess of acid.

In all cases a considerable amount of anil was observed. This was true even when the ratio of chloride to aniline was as great as one molecule to eight or ten. The reactions involved are :



On the whole, the reaction seemed to be the most satisfactory in chloroform solution, the main objection being, that owing to the simultaneous presence of chloroform, alkali, and a trace of aniline, phenyl isocyanide is always formed, and renders the work more or less unpleasant.

A number of experiments were also made to see if the yield could be increased by employing a modification of the Schotten-Bauman reaction¹ for formation of anilids. For this purpose an ethereal solution of the chloride was added to a like solution of aniline, in which was suspended anhydrous potassium carbonate. The proportions of the substances were those demanded by the equation



Very little anilid was, however, obtained, but in its place a substance soluble in water, of acid reaction, capable of forming salts and yielding several well characterized derivatives.

¹ Ber. d. chem. Ges., 17, 2545; 23, 3430.

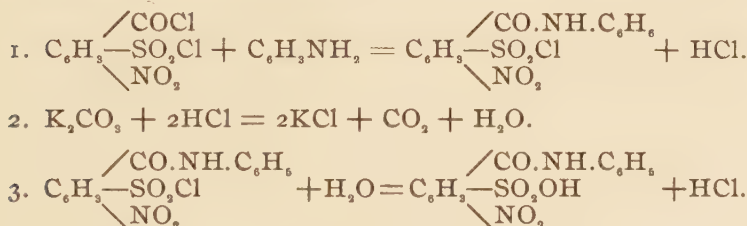
These I hope to study more carefully at some future time.

The acid substance appeared to be an anilido acid, as analyses of its barium salt were obtained which indicated this. The salt was extremely soluble, crystallizing when the solution had gone nearly to dryness, in thick radiating needles. Only a small amount was obtained, and it was undoubtedly impure, but it pointed rather unmistakably to the substance suggested. The analysis was:

0.2225 gram salt lost 0.0405 gram H_2O and gave 0.0530 gram $BaSO_4$.

Calculated for		
	$[C_6H_5-\begin{smallmatrix} \diagup CO.NH.C_6H_5 \\ SO_2O \\ \diagdown NO_2 \end{smallmatrix}]_2$	Ba + $9\frac{1}{2}H_2O$.
Ba	14.42	14.00
H_2O	18.00	18.20

There was of course no evidence as to which acid group combines with the aniline residue. The formation of this substance could be explained by the following reactions:



The anilid is rather sparingly soluble in alcohol, from which it is deposited, on cooling, in microscopic needles. These melt, as stated by Gray, at 222° . It is also soluble in chloroform, ether, and glacial acetic acid, but does not form well defined crystals from any solvent. It is soluble in alkali and is reprecipitated by acids unchanged.

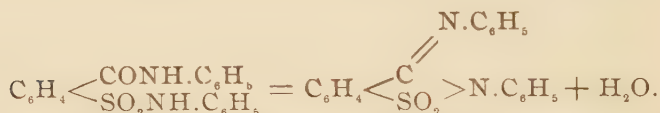
The anil is also soluble in alcohol, glacial acetic acid, etc. It crystallizes in much better formed needles than does the anilid. These melt at 183° . On boiling the anil for some time with aniline it is converted into the anilid,



In none of these reactions was any infusible anilid observed.

IX. THE ACTION OF PHOSPHORUS OXYCHLORIDE ON THE FUSIBLE ANILID.

Hunter¹ found that when either of the anilids of orthosulphobenzoic acid were treated with phosphorus oxychloride, or similar dehydrating agents, a molecule of water was abstracted with the formation of a new substance. A careful study of the compound led to the belief that it was a dianil, and that its formation and structure may be expressed in the following equation :



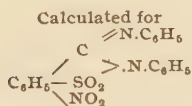
A corresponding study of the fusible anilid of paranitroorthosulphobenzoic acid was undertaken. The method employed in this study was as follows. A tabulated retort of convenient size was fused onto the inner tube of a small condenser. This was done to avoid connections which are nearly always attacked by phosphorus oxychloride. Another satisfactory plan is to have the neck of the retort of the same size as the inner tube of the condenser. The ends are placed in contact and the tubes bound in position by wrappings of asbestos paper. Over the joint so made a tight rubber tube is drawn.

A convenient amount (50 cc.) of phosphorus oxychloride was placed in the retort, and the anilid (5 grs.) added through the tubulus. On boiling with inverted condenser, the anilid soon dissolved with evolution of hydrochloric acid, and the solution became yellow or orange in color. The boiling was continued as long as hydrochloric acid was evolved. The oxychloride was then distilled off under diminished pressure, care being taken to shake the retort constantly during the distillation, as toward the end of the operation there is a tendency to bump violently, if the precaution is omitted. The product remaining, spattered over the walls of the retort, is a greenish yellow solid. Water was then added, and the whole allowed to stand for a few hours to thoroughly dissolve the

¹ Am. Chem. J., 18, 810.

phosphoric acid formed in the reaction. In case the anilid is not perfectly dry, a more energetic reaction occurs, and on distilling off the oxychloride, the product remains as a dark, gummy substance. This should be spread over the sides of the retort while still warm. On cooling, water is added, and gradually the gum disappears, and in its place is found the same yellow product just described. After drying this substance it can be crystallized from acetone, benzene, or glacial acetic acid, after purification with bone-black. From these solvents it crystallizes in small yellow needles resembling quinone in appearance. From acetone the needles are more orange in color than those from glacial acid, apparently because of their greater compactness. In case glacial acid is used, care should be taken to avoid unnecessary heating, as continued boiling with this reagent causes a decomposition which will be spoken of presently. These needles melt at 208° . Analysis gave the following results :

- I. 0.3822 gram gave 0.8334 gram CO_2 and 0.1272 gram H_2O .
 II. 0.2645 " " 0.5812 " " " 0.0910 " "
 III. 0.2023 " " 0.1283 " BaSO_4 (Liebig).
 IV. 0.2061 " " 0.1280 " " "
 V. 0.1853 " " 16.73 cc. N. (standard).



		I.	II.	Found. III.	IV.	V.
C	60.11	59.47	59.93			
H	3.44	3.69	3.82			
S	8.45			8.70	8.52	
N	11.08					11.35

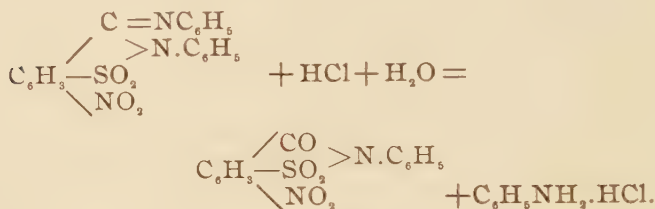
For analyses I and II, I am indebted to Mr. Nakaseko, of this laboratory, who kindly made them for me.

X. THE ACTION OF REAGENTS UPON THE DIANIL OF PARANITROORTHOSULPHOBENZOIC ACID.

1. *The Action of Hydrochloric Acid on the Dianil.*

When the dianil is boiled for some time with concentrated hydrochloric acid the yellow color of the substance disappears

and the dianil is converted into a colorless substance, without, however, passing into solution. The substance so formed, after crystallization from alcohol, was obtained in the form of small colorless needles. They melted at 183° , and possessed all the properties of the anil, which, in fact, they proved to be. The reaction may be thus expressed :



This reaction also explains the fact that some anil was always obtained in making the dianil from the anilid. Hydrochloric acid is formed in the reaction, and in turn reacts with some of the dianil in the sense of the equation just given.

2. *The Action of Alcoholic Potash on the Dianil.*

On boiling the dianil with alcoholic potash for a time, the solution turned red, and nothing but tarry products were obtained. In this respect the dianil differs from the dianil of orthosulphobenzoic acid which, under similar conditions, is transformed into infusible anilid. This observation is, however, in accord with the fact that the nitro derivative is in general much less stable in the presence of alkali.

3. *The Action of Glacial Acetic Acid upon the Dianil.*

When the dianil is boiled with glacial acetic acid for some time, the color of the solution changes to a much lighter shade of yellow, or disappears. On evaporating the solution to small volume and allowing the solution to cool, a colorless substance separates. This is infusible anilid. It could not be obtained in crystals from any solvent, but always separated in flakes. It does not melt or undergo change at 340° . Like the fusible anilid it is soluble in alkali, but on acidifying the solution it does not at once reappear. On standing for some time however, it gradually separates in perfectly pure form. In this

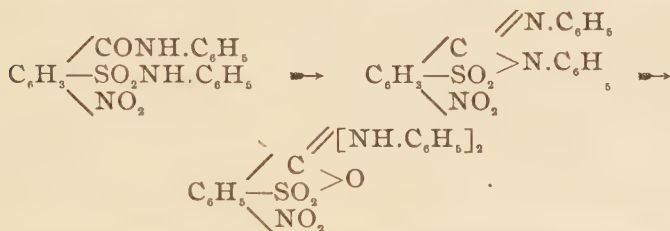
particular my observation differs from that of Gray,¹ who states that this anilid is decomposed by solution in alkali.

A sample that had been repeatedly precipitated gave the following results on analysis :

- I. 0.1607 gram gave 13.88 cc. N (standard).
 II. 0.2195 " " 0.1285 gram BaSO₄.
 III. 0.1357 " " 0.0807 " "

Calculated for C ₆ H ₅ -C(NH.C ₆ H ₅) ₂ SO ₂ >O NO ₂				
		I.	Found. II.	III.
N	10.58	10.85		
S	8.06		8.00	8.16

By this series of transformations, therefore, it is possible to pass from one anilid to the other, the successive steps being :



This is of especial interest as affording a method of passing from a derivative of the symmetrical chloride to a substance derived from the unsymmetrical chloride by steps that can be clearly followed.

CONCLUSIONS.

In the course of this investigation several facts have been established :

1. By the methods described the symmetrical chloride of paranitroorthosulphobenzoic acid can be obtained in fine crystalline condition perfectly free from its unsymmetrical isomer, with an average yield of 40 per cent.

2. By treatment of the chloride with benzene and aluminum chloride only one chlorine atom can be replaced by the phenyl group.

3. The barium salt of paranitroorthobenzoylbenzenesulphonic acid, when perfectly pure, crystallizes constantly with seven molecules of water of crystallization.

¹ Inaug. Dis., J. H. U., 1895.

4. With alcohols the symmetrical chloride yields directly the acid ethereal salt of paranitroorthosulphobenzoic acid, no evidence of an intermediate chloro-ethereal salt having been observed.

5. With phenols two series of derivatives are obtained.

(1) With monohydroxyphenols, both ethereal salts and sulphonphthaleïns are formed, the former predominating.

(2) With polyhydroxyphenols no ethereal salts were obtained, but compounds of the unsymmetrical type, usually containing more than two phenol residues.

6. With aniline an anil, and an anilid of symmetrical constitution, are formed.

7. With phosphorus oxychloride the anilid, by loss of water, forms a dianil.

8. This dianil undergoes transformation with

(1) Glacial acetic acid forming an anilid of unsymmetrical constitution.

(2) Hydrochloric acid forming the anil.

(3) Alcoholic potash, with the formation of colored decomposition products.

BIOGRAPHICAL.

The author of the foregoing dissertation was born at Wilkinsburg, Pa., Jan. 29, 1870. Owing to prolonged sickness in childhood his education prior to entering college was much interrupted, and was largely confined to instruction received at home.

In the fall of 1887 he entered Wooster University (Ohio), from which institution he received the degree of Bachelor of Arts in 1891. The two following years were spent as a teacher of sciences in the College of Emporia (Kansas). In 1893 he entered the Johns Hopkins University, where he has since been pursuing courses in chemistry, with physics and mathematics as subordinate studies.

In 1895 he was appointed University Scholar in Chemistry. During 1895-6 he served as lecture assistant to Prof. Remsen and Dr. Renouf in the undergraduate courses. In the spring of 1896 he was appointed Fellow for the present year.

